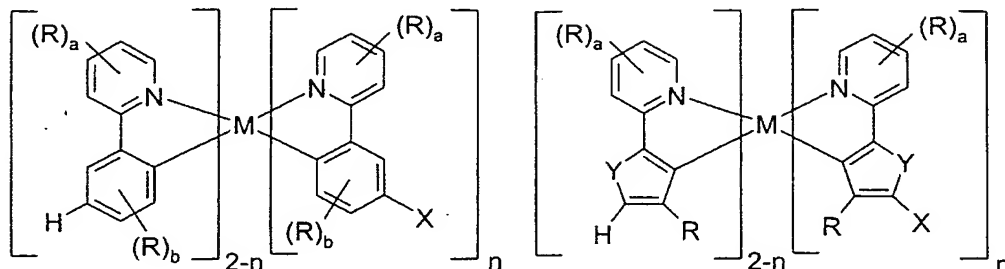


What is claimed is:

1. A compound of the formula (1) and (2)



5 compounds (1)

compounds (2)

where the symbols and indices are each defined as follows:

M is Pd, Pt;

X is Cl, Br, I;

10 Y is O, S, Se, NR¹;

R is the same or different at each instance and is H, F, Cl, Br, I, NO₂, CN, a straight-chain or branched or cyclic alkyl or alkoxy group having 1 to 20 carbon atoms, in which one or more nonadjacent CH₂ groups may be replaced by -O-, -SiR¹₂-, -S-, -NR¹- or -CONR¹- and in which one or more hydrogen atoms may be replaced by F, or an aryl or heteroaryl group having from 4 to 14 carbon atoms which may be substituted by one or more nonaromatic R radicals, and a plurality of R substituents, either on the same ring or on the two different rings, may together in turn form one further aliphatic or aromatic, mono- or polycyclic ring system;

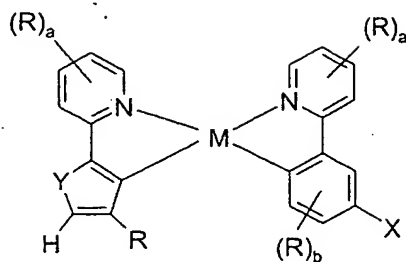
25 R¹ are the same or different at each instance and are each H or an aliphatic or aromatic hydrocarbon radical having from 1 to 20 carbon atoms;

a is 0, 1, 2, 3 or 4;

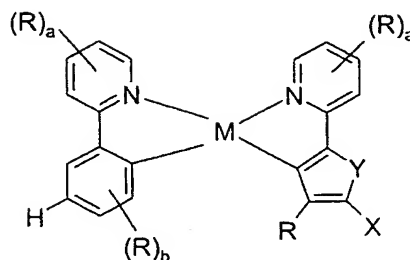
b is 0, 1, 2 or 3;

30 n is 1 or 2.

2. A compound of the formula (1a) and (2a)



compounds (1a)

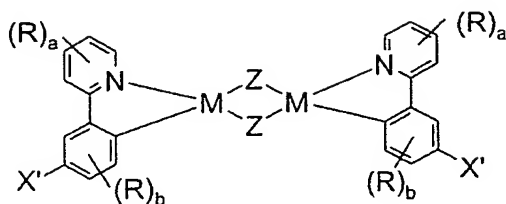


compounds (2a)

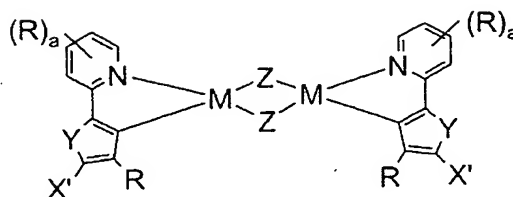
where the symbols and indices are each defined as follows:

- 5 M is Pd, Pt;
 X is Cl, Br, I;
 Y is O, S, Se, NR¹;
 R is the same or different at each instance and is
 H, F, Cl, Br, I, NO₂, CN, a straight-chain or
 10 branched or cyclic alkyl or alkoxy group having 1
 to 20 carbon atoms, in which one or more
 nonadjacent CH₂ groups may be replaced by -O-,
 -SiR¹₂-, -S-, -NR¹- or -CONR¹- and in which one or
 15 more hydrogen atoms may be replaced by F, or an
 aryl or heteroaryl group having from 4 to 14
 carbon atoms which may be substituted by one or
 more nonaromatic R radicals, and a plurality of R
 substituents, either on the same ring or on the
 two different rings, may together in turn form one
 20 further aliphatic or aromatic, mono- or polycyclic
 ring system;
 R¹ are the same or different at each instance and are
 each H or an aliphatic or aromatic hydrocarbon
 radical having from 1 to 20 carbon atoms;
 25 a is 0, 1, 2, 3 or 4;
 b is 0, 1, 2 or 3.

3. A compound of the formula (3) and (4)



compounds (3)



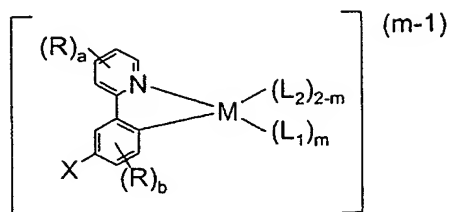
compounds (4)

where the symbols and indices are each defined as follows:

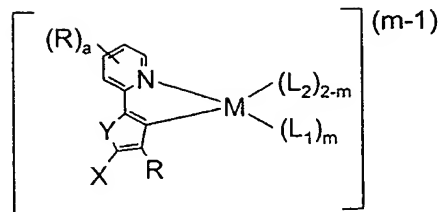
- M is Pd, Pt;
- X' is H, Cl, Br or I, with the proviso that at least one X' per formula is selected from Cl, Br or I;
- Y is O, S, Se, NR¹;
- 10 Z is identically F, Cl, Br, I, O-R¹, S-R¹, N(R¹)₂
- R is the same or different at each instance and is H, F, Cl, Br, I, NO₂, CN, a straight-chain or branched or cyclic alkyl or alkoxy group having 1 to 20 carbon atoms, in which one or more nonadjacent CH₂ groups may be replaced by -O-, -SiR¹₂-, -S-, -NR¹- or -CONR¹- and in which one or more hydrogen atoms may be replaced by F, or an aryl or heteroaryl group having from 4 to 14 carbon atoms which may be substituted by one or more nonaromatic R radicals, and a plurality of R substituents, either on the same ring or on the two different rings, may together in turn form one further aliphatic or aromatic, mono- or polycyclic ring system;
- 20 R¹ are the same or different at each instance and are each H or an aliphatic or aromatic hydrocarbon radical having from 1 to 20 carbon atoms;
- a is 0, 1, 2, 3 or 4;
- b is 0, 1, 2 or 3.

30

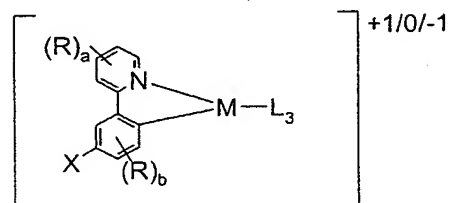
4. A compound of the formula (5), (6), (7) and (8),



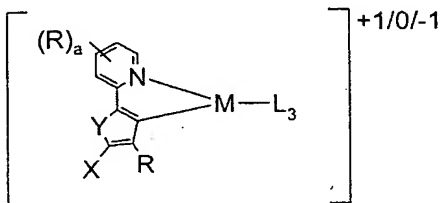
compounds (5)



compounds (6)



compounds (7)



compounds (8)

5 where the symbols and indices are each defined as follows:

M is Pd, Pt;

X is Cl, Br, I;

Y is O, S, Se, NR¹;

10 R is the same or different at each instance and is H, F, Cl, Br, I, NO₂, CN, a straight-chain or branched or cyclic alkyl or alkoxy group having 1 to 20 carbon atoms, in which one or more nonadjacent CH₂ groups may be replaced by -O-,
 15 -SiR¹₂-, -S-, -NR¹- or -CONR¹- and in which one or more hydrogen atoms may be replaced by F, or an aryl or heteroaryl group having from 4 to 14 carbon atoms which may be substituted by one or more nonaromatic R radicals, and a plurality of R
 20 substituents, either on the same ring or on the two different rings, may together in turn form one further aliphatic or aromatic, mono- or polycyclic ring system;

R¹ are the same or different at each instance and are
 25 each H or an aliphatic or aromatic hydrocarbon radical having from 1 to 20 carbon atoms;

L₁ is an uncharged, monodentate ligand;

L₂ is a monoanionic, monodentate ligand;

L₃ is an uncharged or mono- or dianionic bidentate
 30 ligand;

a is 0, 1, 2, 3 or 4;

b is 0, 1, 2 or 3;
m is 0, 1 or 2.

5. A compound as claimed in claim 4, characterized in
5 that L₁ is carbon monoxide, an isonitrile, for example,
in particular, tert-butylisonitrile, cyclohexyl-
isonitrile, adamantylisonitrile, an amine, in
particular, for example, trimethylamine, triethylamine,
morpholine, phosphines, for example trifluorophosphine,
10 or else aliphatic, aromatic or heteroaromatic
phosphines, in particular trimethylphosphine,
tricyclohexylphosphine, dicyclohexylphenylphosphine,
tri-o-tolylphosphine, tri-tert-butylphosphine, tri-
phenylphosphine, tris(pentafluorophenyl)phosphine or
15 trifluorophosphine, phosphites, in particular, for
example, trimethyl phosphite, triethyl phosphite,
arsines, in particular, for example, trifluoroarsine,
trimethylarsine, tricyclohexylarsine, tri-tert-
butylarsine, triphenylarsine, tris(pentafluorophenyl)-
20 arsine, stibines, in particular, for example,
trifluorostibine, trimethylstibine, tricyclohexyl-
stibine, tri-tert-butylstibine, triphenylstibine,
tris(pentafluorophenyl)stibine or a nitrogen-containing
heterocycle, in particular pyridine, pyridazine,
25 pyrazine, triazine.

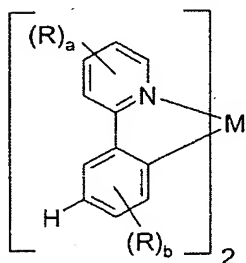
6. A compound as claimed in claim 4, characterized in
that L₂ is a halide, in particular F, Cl, Br, I, or
cyanide, cyanate, isocyanate, thiocyanate, isothio-
30 cyanate, an alkoxide, in particular, for example,
methoxide, ethoxide, propoxide, isopropoxide, tert-
butoxide, phenoxide, a thioalkoxide, in particular, for
example, methanethiolate, ethanethiolate, propane-
thiolate, isopropanethiolate, tert-thiobutoxide,
35 thiophenoxide, an amide, in particular, for example,
dimethylamide, diethylamide, diisopropylamide, a
carboxylate, in particular, for example, acetate,
trifluoroacetate, propionate, benzoate, or an anionic
nitrogen-containing heterocycle, in particular

morpholide, pyrrolide, imidazolide, pyrazolide.

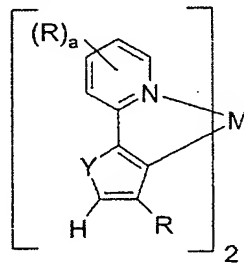
7. A compound as claimed in claim 4, characterized in that L_3 is a diamine, in particular, for example, 5 ethylenediamine, N,N,N',N' -tetramethylethylenediamine, propylenediamine, N,N,N',N' -tetramethylpropylene-
diamine, cis-, trans-diaminocyclohexane, cis-, trans-
10 N,N,N',N' -tetramethyldiaminocyclohexane, imines, in particular, for example, 2[(1-(phenylimino)ethyl)-
pyridine, 2[(1-(2-methylphenylimino)ethyl)pyridine, 2[(1-(2,6-diisopropylphenylimino)ethyl)pyridine,
2[(1-methylimino)ethyl]pyridine, 2[(1-(ethylimino)-
ethyl]pyridine, 2[(1-(isopropylimino)ethyl]pyridine,
15 2[(1-(tert-butylimino)ethyl]pyridine, diimines, in particular, for example, 1,2-bis(methylimino)ethane,
1,2-bis(ethylimino)ethane, 1,2-bis(isopropylimino)-
ethane, 1,2-bis(tert-butylimino)ethane, 2,3-bis(methyl-
imino)butane, 2,3-bis(ethylimino)butane, 2,3-bis(iso-
propylimino)butane, 2,3-bis(tert-butylimino)butane,
20 1,2-bis(phenylimino)ethane, 1,2-bis(2-methylphenyl-
imino)ethane, 1,2-bis(2,6-diisopropylphenylimino)-
ethane, 1,2-bis(2,6-di-tert-butylphenylimino)ethane,
2,3-bis(phenylimino)butane, 2,3-bis(2-methylphenyl-
imino)butane, 2,3-bis(2,6-diisopropylphenylimino)-
25 butane, 2,3-bis(2,6-di-tert-butylphenylimino)butane,
heterocycles containing two nitrogen atoms, in particular, for example, 2,2'-bipyridine,
o-phenanthroline, diphosphines, in particular, for example, bis-diphenylphosphinomethane, bisdiphenyl-
30 phosphinoethane, bis(diphenylphosphino)propane, bis(di-
methylphosphino)methane, bis(dimethylphosphino)ethane,
bis(dimethylphosphino)propane, bis(diethylphosphino)-
methane, bis(diethylphosphino)ethane, bis(diethyl-
phosphino)propane, bis(di-tert-butylphosphino)methane,
35 bis(di-tert-butylphosphino)ethane, bis(tert-butyl-
phosphino)propane, 1,3-diketonates derived from
1,3-diketones, in particular, for example, acetylacetone, benzoylacetone, 1,5-diphenylacetyl-
acetone, dibenzoylmethane, bis(1,1,1-trifluoro-

acetyl)methane, 3-ketonates derived from 3-keto esters, in particular, for example, ethyl acetoacetate, carboxylates derived from aminocarboxylic acids, in particular, for example, pyridine-2-carboxylic acid, quinoline-2-carboxylic acid, glycine, dimethylglycine, alanine, dimethylaminoalanine, salicyliminates derived from salicylimines, in particular, for example, methylsalicylimine, ethylsalicylimine, phenylsalicylimine, dialkoxides derived from dialcohols, in particular, for example, ethylene glycol, 1,3-propylene glycol, dithiolates derived from dithiols, in particular, for example, 1,2-ethylenedithiol, 1,3-propylenedithiol, heteroarylborate, in particular, for example, tetrakis(1-imidazolyl)borate, tetrakis(1-pyrazolyl)borate.

8. A process for preparing the compounds defined in claim 1, by reacting the compounds (9) or (10)



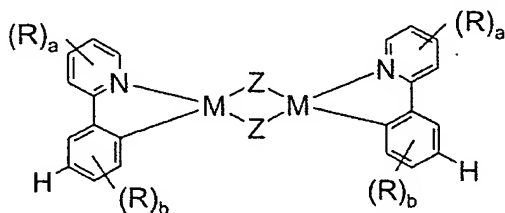
compounds (9)



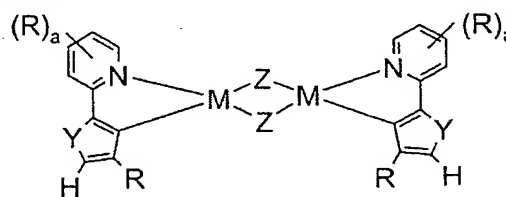
compounds (10)

in which M and the radicals and indices Y, R, R¹, a and b are each as defined in claim 1 with halogenating agents and subsequently reducing them.

9. A process for preparing the compounds defined in claim 3, by reacting the compounds (11) or (12)



compounds (11)

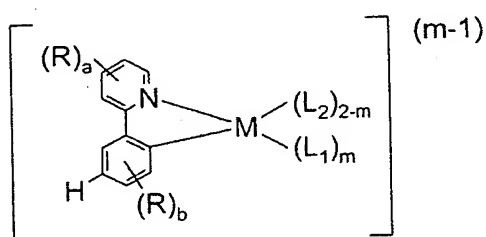


compounds (12)

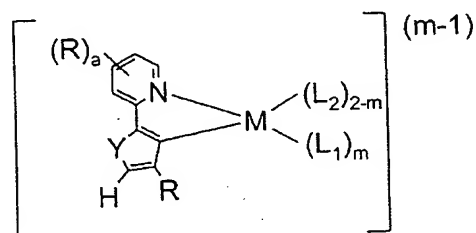
in which M and the radicals and indices Z, Y, R, R¹, a and b are each as defined in claim 3 with halogenating

agents and subsequently reducing them.

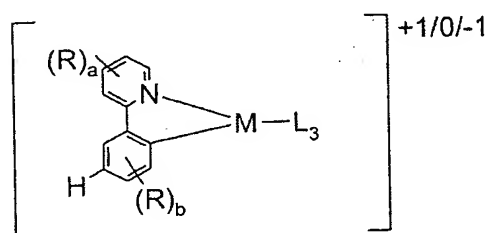
10. A process for preparing the compounds defined in claim 4, by reacting the compounds (13), (14), (15) or (16),



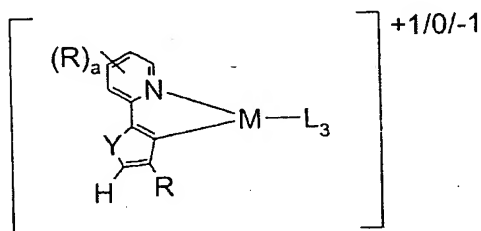
compounds (13)



compounds (14)



compounds (15)



compounds (16)

- 10 in which M and the radicals and indices L_1 , L_2 , L_3 , Y, R, R^1 , a, b and m are each as defined above with halogenating agents and subsequently reducing them.

11. The process as claimed in one or more of claims 8 to 10, characterized in that the halogenating agent used is a halogen X_2 or an interhalogen X-X and a base in a molar ratio of from 1:1 to 1:100, or an organic bromine complex such as pyridinium perbromide, and in each case optionally a Lewis acid in a molar ratio (halogen to Lewis acid) of from 1:0.1 to 1:0.0001.

12. The process as claimed in one or more of claims 8 to 10, characterized in that the halogenating agent used is an organic N-Hal compound.

13. The process as claimed in one or more of claims 8 to 10, characterized in that the halogenating agent used comprises organic O-Hal compounds and halogens X_2 in a molar ratio of from 0.5:1 to 1:1.

14. The process as claimed in one or more of claims 8 to 10, characterized in that a stoichiometric ratio of the halogenating agents as claimed in claims 11 to 13, based on the content of active halogen, to the compounds (9), (10), (11), (12), (13), (14), (15) or (16) of 2:1 is used.

15. The process as claimed in one or more of claims 8 to 10, characterized in that a stoichiometric ratio of the halogenating agents as claimed in claims 11 to 13, based on the content of active halogen, to the compounds (9), (10), (11), (12), (13), (14), (15) or (16) of from 3:1 to 1000:1 is used.

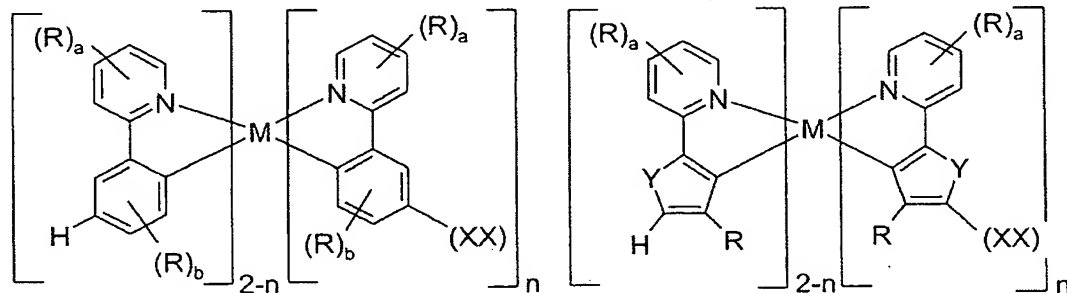
16. The process as claimed in one or more of claims 8 to 15, characterized in that a reducing agent is added to the reaction mixture in a molar ratio of from 1:1 to 10 000:1 based on the compounds (9), (10), (11), (12), (13), (14), (15) or (16), and the addition is effected simultaneously with the addition of the halogenating agents (I), (II) or (III), or after a time delay.

17. The process as claimed in one or more of claims 8 to 16, characterized in that the reducing agent used is hydrazine (hydrate) or salts thereof, hydroxylamine or salts thereof, hydroxylamine-O-sulfonic acid and hydroquinones, alkali metal and alkaline earth metal sulfites, alkali metal and alkaline earth metal dithionites, alkali metals and alkaline earth metals and their amalgams and other corresponding alloys, transition metals such as manganese, iron, nickel and zinc, and transition metal alloys.

18. The process as claimed in one or more of claims 8 to 15, characterized in that the reduction may also be effected by dry-heating, under reduced pressure, the palladium(IV) or platinum(VI) compounds which have been formed as intermediates and isolated in substance.

19. A compound as claimed in one or more of claims 1 to 4, characterized in that its purity (determined by means of ^1H NMR or HPLC) is more than 99%.

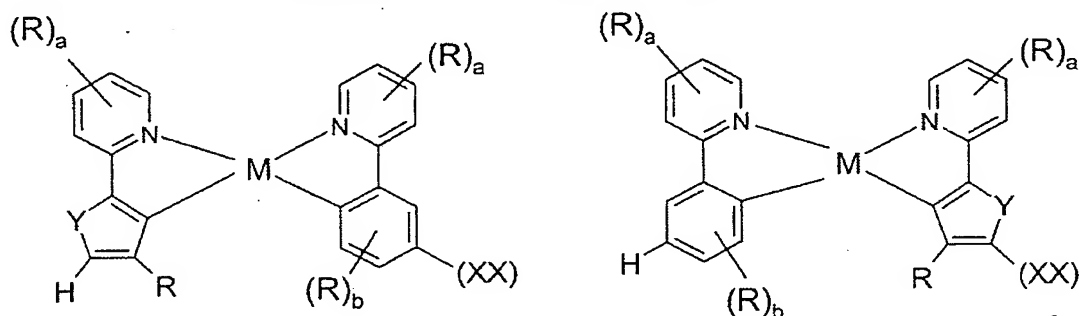
5 20. A conjugated or semiconjugated or nonconjugated polymer containing one or more compounds of the formula (1') and/or (2')



compounds (1')

compounds (2')

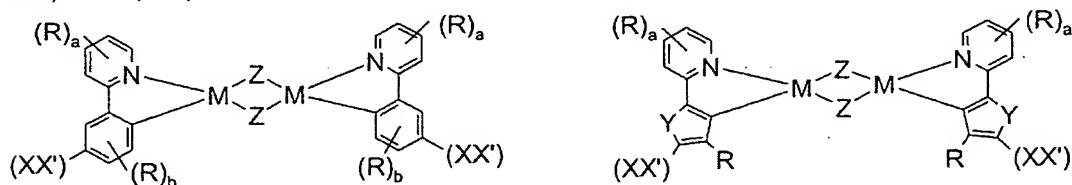
10 and/or of the formula (1a') and/or (2a')



compounds (1a')

compounds (2a')

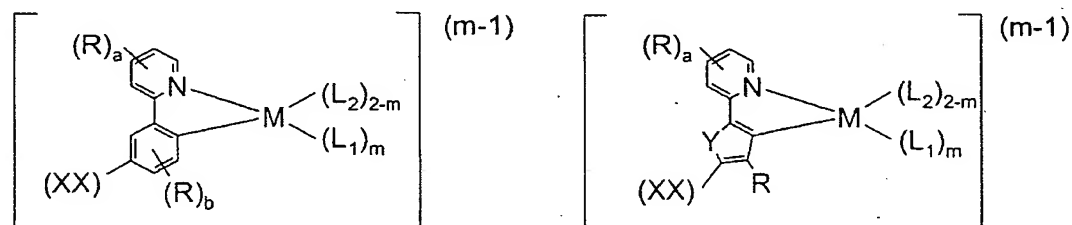
and/or of the formula (3'), (4'), (5'), (6'), (7') and/or (8')



15

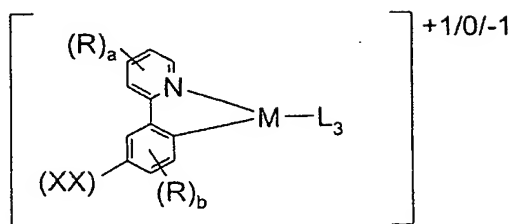
compounds (3')

compounds (4')

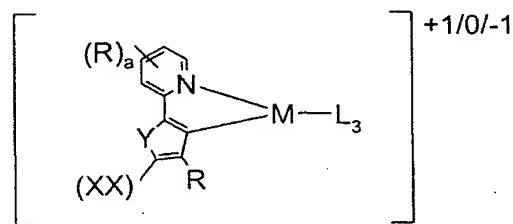


compounds (5')

compounds (6')



compounds (7')



compounds (8')

where the symbols and indices are each defined as follows:

- 5 M is Pd, Pt;
 Y is O, S, Se, NR¹;
 R is the same or different at each instance and is H, F, Cl, Br, I, NO₂, CN, a straight-chain or branched or cyclic alkyl or alkoxy group having 1
 10 to 20 carbon atoms, in which one or more nonadjacent CH₂ groups may be replaced by -O-, -SiR¹₂-, -S-, -NR¹- or -CONR¹- and in which one or more hydrogen atoms may be replaced by F, or an aryl or heteroaryl group having from 4 to 14
 15 carbon atoms which may be substituted by one or more nonaromatic R radicals, and a plurality of R substituents, either on the same ring or on the two different rings, may together in turn form one further aliphatic or aromatic, mono- or polycyclic
 20 ring system;
 R¹ are the same or different at each instance and are each H or an aliphatic or aromatic hydrocarbon radical having from 1 to 20 carbon atoms;
 L₁ is an uncharged, monodentate ligand;
 25 L₂ is a monoanionic, monodentate ligand;
 L₃ is an uncharged or mono- or dianionic bidentate ligand;
 a is 0, 1, 2, 3 or 4;
 b is 0, 1, 2 or 3;
 30 m is 0, 1 or 2;
 n is 1 or 2;
 (XX) is a bond to the conjugated or semiconjugated or nonconjugated polymer;
 (XX') is H or a bond to the conjugated or

semiconjugated or nonconjugated polymer, but at least one (XX') per formula is a bond to the conjugated or semiconjugated or nonconjugated polymer.

- 5 21. A polymer as claimed in claim 20, characterized in that it has been obtained using one or more compounds of the formula (1), (1a), (2), (2a) and/or (3) to (8) defined in claims 1 to 4.
- 10 22. A polymer as claimed in claims 20 and/or 21, characterized in that the polymer contains repeat units taken from polyfluorenes, polyspirobifluorenes, poly-para-phenylenes, polycarbazoles or polythiophenes.
- 15 23. A polymer as claimed in one or more of claims 20 to 22, characterized in that the polymer is a homo- or copolymer.
- 20 24. A polymer as claimed in one or more of claims 20 to 23, characterized in that the polymer is soluble in organic solvents.
- 25 25. An electronic component comprising at least one compound as claimed in one or more of claims 1 to 4.
26. An electronic component comprising at least one polymer as claimed in one or more of claims 20 to 24.
- 30 27. An electronic component, characterized in that it comprises organic or polymeric light-emitting diodes (OLEDs or PLEDs), organic integrated circuits (O-ICs), organic field-effect transistors (OFETs), organic thin-film transistors (OTFTs), organic solar cells (O-SCs) or else organic laser diodes (O-lasers).

Abstract

Palladium and platinum complexes

The present invention relates to new types of organometallic compounds which are phosphorescence emitters. Such compounds can be used as active components (= functional materials) in a series of different types of application which can be classed within the electronics industry in the broadest sense.

The inventive compounds are described by the formulae (1), (1a), (2), (2a), (3), (4), (5), (6), (7) and (8).